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(54) THERMALLY REVERSIBLE MULTIPLE COLOR RECORDING MEDIUM

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a new reversible multiple color recording medium by which a more accurate, finer and clearer multiple color image can be expressed, and wherein a re-writing can be freely performed by deleting the image.

SOLUTION: A writing is performed by using at least three laser beams, and this thermally reversible multiple color recording medium is constituted by laminating at least following three layers of respective thermally reversible color recording layers (A) to (C) on a base sheet 5. That is, the thermally reversible multiple color recording medium comprises (A) a thermally reversible color recording layer 1 comprising a first thermally reversible color developing layer 1a and a first laser

beam absorbing layer 1b having a wavelength to develop a color of the color developing layer, (B) a thermally reversible color recording layer 2 comprising a second thermally reversible color developing layer 2a and a second layer beam absorbing layer 2b having a wavelength to develop a color of the color developing layer, and (C) a thermally reversible color recording layer 3 comprising a third thermally reversible color developing layer 3a and a third laser beam absorbing layer 3b having a wavelength to develop a color of the color developing layer. More preferably, a transparent heat insulating layer (glass bead or the like) is inserted between the recording layers 1 and 2, and 2 and 3. A multiple color recording/deletion is performed with colors of red, blue, green and the like.

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CLAIMS

[Claim(s)]

[Claim 1] The heat-reversibility multicolor record medium characterized by coming to carry out the laminating of the three layers of each heat reversible color recording layer of following (A) - (C) at least on a substrate (5).

(A) The heat reversible color recording layer which consists of the 1st heat reversible color coloring layer (1a) and an absorption layer (1b) of the 1st laser beam which has the wavelength for coloring of this coloring layer (1)

(B) The heat reversible color recording layer which consists of an absorption layer (2b) of the 2nd laser beam which has the wavelength for coloring of the 2nd heat reversible color coloring layer (2a) and this coloring layer (2)

(C) The heat reversible color recording layer which consists of the 3rd heat reversible color coloring layer (3a) and an absorption layer (3b) of the 3rd laser beam which has the wavelength for coloring of this coloring layer (3)

[Claim 2] The heat-reversibility multicolor record medium characterized by coming further to carry out the laminating of the transparence thermal break (4) between the layers of the heat reversible color recording layer (1, 2, 3) of at least three layers by which a laminating is carried out in said claim 1.

[Claim 3] The heat-reversibility multicolor record medium according to claim 2 which said transparence thermal break (4) becomes with the detailed glass bead implanted in the shape of a dot by 5-100 micrometers in thickness.

[Claim 4] The heat-reversibility multicolor record medium according to claim 1 or 2 with which the hue in said each heat reversible color coloring layer (1a, 2a, 3a) consists of red, blue, and one of three green colors.

[Claim 5] A heat-reversibility multicolor record medium given in claims 1 and 2 as which said each laser beam is chosen from light with a wavelength of 600-1000nm emitted from semiconductor laser, or any 1 term of 4.

[Claim 6] A heat-reversibility multicolor record medium given in claims 1, 2, and 4 which the absorption layer (1b, 2b, 3b) of each of said laser beam is respectively chosen from with a molar extinction coefficients of 10000 or more infrared absorption agents, and come to contain this, or any 1 term of 5.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] Especially this invention relates to the improved heat-reversibility multicolor record medium suitable for laser writing. This self can be used for the various advertising media whose rewriting is possible, or this record medium can also coalesce and use it for rewriting or the various possible cards of a reuse.

[0002]

[Description of the Prior Art] general -- a reversibility record medium -- the Society of Electrophotography of Japan -- there are two, the case where an image expression is carried out in the monochrome of only nebula by making a physical change into a principle, and when an image expression is carried out with multiple color by making a chemical change into a principle, so that it may be, even if special edition description is given as "latest trend of a RIRAITA bloomers king technique" at volume [35th] No. 3 (1996) and 148-154 pages. Although this is made into a card system and it has already used in the reversibility (lilac ITABURU) record medium by the former monochrome in 1 section gas station etc., the present condition is not being the phase of practical use yet in the reversibility record medium by the latter multiple color. It is thought that research is advanced and they go as a future big theme since the needs of colorization are high.

[0003] JP,8-80682,A can be mentioned as a technique in recent years seen by patent application about a reversibility multicolor record medium. The basic technical thought of this official report uses as a lower layer the coloring layer which consists of one layer containing two or more irreversible colors (the color or the organic pigment currently generally used for printing ink) which absorb a wavelength light peculiar to the color respectively, and generate heat, carries out the laminating of the lilac ITABURU layer reversibly changed on it at transparence or non-transparence (nebula) at specific temperature (temperature by generation of heat of this irreversible color), and is taken as a reversibility multicolor record medium. The coloring layer which consists of this one layer here is divided into each pigmented layer, this lilac ITABURU layer is prepared on it for every pigmented layer, the laminating of this is respectively carried out through the thermal break (air) of translucency, and the purport good also as this record medium is also indicated.

[0004]

[Problem(s) to be Solved by the Invention] this invention persons have examined many things from another different include angle from said number official report. Consequently, the reversibility multicolor record medium which was excellent also in endurance in a clearer multi-colored picture image being could be found out, and this invention was reached.

[0005]

[Means for Solving the Problem] That is, this invention makes a main means the heat-reversibility multicolor record medium which the laminating of the three layers of each heat reversible color recording layer of following (A) - (C) is carried out, and becomes at least on a substrate (5) so that it may indicate to claim 1 first.

(A) The heat reversible color recording layer which consists of the 1st heat reversible color coloring layer (1a) and an absorption layer (1b) of the 1st laser beam which has the wavelength for coloring of this coloring layer (1)

(B) The heat reversible color recording layer which consists of an absorption layer (2b) of the 2nd laser beam which has the wavelength for coloring of the 2nd

heat reversible color coloring layer (2a) and this coloring layer (2)
(C) The heat reversible color recording layer which consists of the 3rd heat reversible color coloring layer (3a) and an absorption layer (3b) of the 3rd laser beam which has the wavelength for coloring of this coloring layer (3)
[0006] And invention of claim 2 is also offered in relation to said main patent. It is the heat-reversibility multicolor record medium characterized by carrying out the laminating of the transparence thermal break (4) further between the layers of said heat reversible color recording layer (1, 2, 3) of at least three layers by which a laminating is carried out. This transparence thermal break (4) prepares as a desirable gestalt here with the detailed glass bead implanted in the shape of a dot by 5-100 micrometers in thickness, and it is **** (claim 3).
[0007] Moreover, invention which is subordinate to said claim 1 or 2, and is indicated to claims 4, 5, and 6 is also offered. This invention is explained in full detail with the following operation gestalt below.
[0008]
[Embodiment of the Invention] First, the heat-reversibility multicolor record medium (it is called a HRC medium below.) of this invention writes in a certain information freely using three laser (light) with which wavelength differs at least, and expresses the written-in information quickly by the image of three or more colors (development). Conversely, if this is quenched at a certain temperature or gradual cooling is carried out, the expression color picture will be maintained as it is, or it will be eliminated. Repeat actuation of this expression and elimination can be performed, that is, it can be said to be what made possible the RIRAITA bull color information record medium by the new configuration.
[0009] Writing is specified as the laser beam especially here as compared with the approach of writing in by the thermal emission from other thermal heads, the MAG, electric field, a pressure, etc., because I hear that a more detailed image can arrange in the state of being written in quickly more vividly and non-contact and there is also no danger, such as dirt and damage.
[0010] Then, based on claim 1, it explains on what kind of configuration the HRC

medium by said at least three laser beams which can be written in is based.
[0011] First, a HRC medium is formed on a substrate 5, in order to make it easy (on manufacture and use) to be safe and to deal with it. The use gestalten (a material, thickness, transparence - opacity, application, etc.) of this substrate are as follows. About a material, inorganic sheet-like objects, such as a sheet-like object by thermosetting resin, such as a sheet-like object by the thermoplastics of crystallinity, such as the paper board, a synthetic paper, the nonwoven fabric by the synthetic fiber, polyethylene terephthalate, polyethylenenaphthalate, a polyether ketone, a polycarbonate, polymethylmethacrylate, annular polyolefine, polyether sulphone, and polyarylate, or amorphism nature, an epoxy system, acrylic, an urethane system, and an imide system, a ceramic, and glass, are mentioned, for example. of course -- these -- proper -- you may be the compound sheet which compounded two or more sorts. Generally such thickness is set to about 0.1-3mm. Moreover, about transparence - (translucent) - opacity, especially this is decided by relation with an application. For example, for applications like a display, such as a poster, an opaque sheet is chosen in coalesce with transparence thru/or a translucent sheet, and various cards. case [and] these are transparent -- no coloring -- it is -- translucent - when opaque, it is desirable that it is a white system. Whitening has approaches, such as a scour lump by titanium oxide or surface coating, and surface roughening. In addition, in order to give an adhesive property to said sheet, you may pretreat by physical (corona discharge etc.) and the chemical approaches (scaling by the oxidizer etc.), and if , an anchor coat layer may be prepared.
[0012] And although the laminating of the heat reversible color recording layer (1) of (A) - (C), (2), and (3) is carried out respectively independently at least on said substrate 5, this is for carrying out an image expression by three colors respectively at least using three laser beams from which wavelength differs at least. Therefore, calling the 1st and (B) the 2nd, and having especially called (C) the 3rd does not call (A) in order [these] to distinguish to three, even if few, and the sequence of a laminating (this recording layer-hue) is not said [expedient],

either. As for the built-up sequence of a **** recording layer, it is desirable to use a dark color system as the lowest layer from the point of improvement, to turn the laminating of the light color up one by one, and to make it consist of that of visibility. For example, in the case of three hues of red, blue, green, or yellow, blue is made the lowest layer and green or yellow is made an interlayer for red at the maximum upper layer.

[0013] Said heat [in / at least / the 1st, the 2nd, and the 3rd] reversible color recording layer (1, 2, 3) consists of a heat reversible color coloring layer (1a, 2a, 3a) and a laser beam absorption layer (1b, 2b, 3b) corresponding to each. Next, each of this pigmented layer from ** and an absorption layer are explained in full detail.

[0014] First, when carry out a color expression by red, blue, and three green hues, said each heat reversible color coloring layer use as a principal component both of the electronic receptiveness compound (it be call a developer below.) which carry out a ****** operation with temperature to the precursor (it be call the color coupler below.) and this color coupler of the electron-donative color which be each source of coloring, it mix this to binder resin, distribute, and make them each ****. For existence of this resin, it is [discharge / coloring and] more desirable for there to be nothing from the field of a clearer and faithful repeat operation here. However, in order to distribute a color coupler and a developer to homogeneity and to make adhesion with a substrate 5 firm, concomitant use of this resin is desirable. However, the thing little as much as possible of the amount of presentations is desirable.

[0015] As said color coupler, they are fluoran lactone compounds, such as 2-clo low 6-diethylamino fluoran lactone and 3-MECHIRU 6-diethylamino fluoran lactone, for example at red. If blue, they are phthalide system compounds, such as 3-(4-diethylamino 2-methylphenyl)-3-(1-ECHIRU 2-methylindole 3-IRU)-4-aza-phthalide and 3-(4-diethylamino 6-ethoxy phenyl)-3-(1-hexyl 2-methylindole 3-IRU)-4-aza-phthalide. If green, they are fluoran lactone compounds, such as 7-(N and N-dibenzylamino)-3-(N and N-diethylamino) fluoran lactone and 7-(N-octyl

amino)-3-(N and N-diethylamino) fluoran lactone. Otherwise, in yellow, fluoran lactone compounds, such as 3-methoxy 6-methoxy fluoran lactone, can be illustrated, and, black, fluoran lactone compounds, such as 7-(2-KURORU phenylamino)-3-(diethylamino) fluoran lactone and 6-methyl-7-(2, 4-dimethyl phenylamino)-3-(diethylamino) fluoran lactone, can be illustrated. Of course, by the ordinary state, these are carrying out colorlessness or light coloring, and differ from the color for ink and pigment which are respectively colored by the ordinary state.

[0016] Moreover, there is especially nothing that will be restricted if said developer is a compound which doubles and has fundamentally a part for a part for the structured division which shows the development ability which makes said color coupler color, and the long-chain aliphatic series structured division which controls the cohesive force between molecules. For example, in a part for the structured division which shows this development ability, it is a phosphoric-acid radical, a carboxylic-acid radical, an aromatic series radical, etc., and is the long-chain alkyl group of C12-C24 preferably ten or more carbon numbers C in a part for the structured division which controls this cohesive force. When a concrete compound is illustrated, an N-BEHENIROIRU 4-aminophenol, p-(octadecyl thio) phenol, p-(eicosyl oxy-) phenol, Long-chain alkyl aromatic series system compounds, such as p-hexadecyl carbamoyl FENIRU and 4-(N-behenoyl amino) phenoxyacetic acid, alpha-hydroxy hexadecanoic acid, 2-BUROMO hexadecanoic acid, 3-oxo-octadecanoic acid, Long-chain alkyl phosphoric-acid compounds, such as long-chain alkyl monochrome, such as an octadecyl malic acid, octadecyl thiophosphoric acid, and 2-octadecyl pen TANIN acid, or a dicarboxylic acid compound, octadecyl phosphonic acid, and eicosyl phosphonic acid, etc. can be mentioned.

[0017] Moreover, it is good to choose [being called the resin which is compatible to a color coupler and a developer as said binder resin first, is excellent in adhesion with a substrate 5, dissolves in a solvent (water or organic solvent), and is excellent also in the transparence of itself, a heatproof, and weatherability].

Although various resin which suits the resin of these conditions is considered, choosing in the thermoplastic polymer of amorphism nature is more desirable.
[0018] The thermoplastic polymer of the amorphism nature as said binder resin For example, the copolymerization polymer of a polyvinyl chloride, polyvinyl acetate, a polyvinyl chloride, and vinyl acetate, Polystyrene or the copolymerization polymer of this and other vinyl monomers, the copolymerization polymer of independent or this acrylic and other acrylic vinyl monomers, Vinyl system polymers, such as a maleic-acid system copolymerization polymer, a polyvinyl alcohol system polymer, and an annular olefin system polymer, A phenoxy polymer, polyurethane, a polycarbonate, an ester system polymer (amorphia), a semisynthesis cellulose (ethyl cellulose, hydroxyethyl cellulose, carboxymethyl cellulose), starch, etc. can be mentioned. In addition, when daring use a crystalline thermoplastic polymer, degree of crystallinity is low as much as possible, and it is good to choose what has the low melting point.
[0019] although the presentation rate of said which color coupler which constitutes said each heat reversible color coloring layer, a developer, and binder resin is good to take various conditions into consideration and for preliminary experiment to determine -- a profile -- it is as follows. 15 - 40 % of the weight of color couplers, 85 - 60 % of the weight of developers, and binder resin are 1 - 10 % of the weight to the total quantity of a color coupler and a developer. In addition, minute amount addition of additives, such as a sensitizer which is used for a dispersant, a surfactant, lubricant, an antioxidant, an ultraviolet ray absorbent, light stabilizer, a coloring stabilizer, a decolorization accelerator, and a common thermal paper for improvements, such as the formation property of this coloring layer and coloring/decolorization property, is permitted.
[0020] And generally as for the means forming to the substrate top of each of said heat reversible color coloring layer, the following approach is taken. The resin binder of the amount of requests is first dissolved in an organic solvent. Since the amount of dissolutions changes with the solubility and the formation approaches for this resin and it is not decided uniquely, it is good to decide by

the preliminary test. Next, separate or the thing ****** mixed is respectively added for the initial complement of a predetermined color coupler and a predetermined developer in the dissolved solution. After addition is fully stirred and distributes the whole to homogeneity. Here, there is no limit in mixed conditions and a mixed sequence foreword. And it applies to predetermined thickness with coating means (SUPINKO-TEINGU, roll coating, ******-**-TENIGU, screen printing, etc.), and dries.

[0021] As for the thickness of each of said coloring layer coated here, it is desirable to change by whether it makes into an interlayer whether to make this into the lowest layer or it is made the maximum upper layer. This is because it will become easy to come to the coloring concentration of the image which worsens transparency of a laser beam and is displayed as a result, the Sharp difference, etc. out of a bad influence if the upper layer is thick. therefore -- ** -- saying and making it too much thin will lower coloring concentration of a layer own [the]. Therefore, although it is good to decide by the prior check with careful attention to this thing, preferably, the range which can generally be said is 5-20 micrometers, and finds out the 1-30 micrometers of the optimal thickness for each coloring layer in this.

[0022] Next, the absorption layer (1b) of the 1st, 2, and 3 laser beam prepared corresponding to said each heat reversible color coloring layer (1a) (2a) (3a), (2b), and (3b) are explained in full detail.

[0023] Said each absorption layer is required for it to be efficient and transmit [absorb quickly the 1st, 2nd, or 3rd laser beam from which wavelength differs respectively, change into heat (predetermined temperature) and] this in each the layer of said coloring faithfully. Therefore, it will be decided by what kind of hue this absorption layer makes this coloring layer, and a laser beam (wavelength) will also be decided. This will also become that this absorption layer and this coloring layer to it decided, if the wavelength of each laser beam to be used is decided conversely. The tint of a **** absorption layer and the tint of a coloring layer are good to make it double as much as possible.

[0024] The laser beam used first here is chosen and it is still better that the wavelength what generally has preferably about 600-1000nm of 650-900nm wavelength regions was decided to be within this wavelength is single wavelength as much as possible. The generation source of a **** laser beam has the desirable semiconductor laser of about 20mW of optical outputs especially, although gas laser, fixed laser, semiconductor laser, etc. are applicable.
[0025] And said each absorption layer to said each decided laser beam is specifically the thing of the following contents. First, this layer is alternatively efficient, absorbs the wavelength from the selected laser beam, and a laser beam absorbent convertible into predetermined heat (temperature) energy as it is serves as a principal component, and it is formed. More effective selection of this absorbent is that it is desirable to also take a molar extinction coefficient into consideration further here, although decided of course in consideration of the effect of the coloring chromaticity on said each decided coloring layer, endurance (thermal resistance to repetitive heating and cooling), film production nature, adhesion with a coloring layer, etc.
[0026] the strength of absorption in the range of 600-1000nm (visible being and carrying out infrared wavelength) where said absorbent molecule is emitted from a laser beam in this invention although said molar extinction coefficient (it is also called a molar extinction coefficient.) is generally expressed as the strength to which a coloring matter molecule absorbs light -- ** -- it will say. And this is JIS. It can measure with the spectrophotometry indicated by K0212. If this molar extinction coefficient is also considered and it will also put [as opposed to / in / this absorbent / figure / 10000 or more laser beam absorbents and the laser beam which are these 20000 or more absorbents more preferably, and is specified further] into conditions that the width of face of an absorption wavelength peak is a thing 200nm or less, a much more desirable infrared absorption agent can be chosen.
[0027] When said target laser beam absorbent is illustrated to a system category, this absorbent that absorbs only thermal-conversion wavelength peculiar to

coloring of said coloring layer based on said conditions further in this will be chosen by the cyanine system generally known, a phthalocyanine system, the India cyanine system, a naphthalocyanine system, an anthraquinone system, a poly methine system, the aminium system, the potato NIUMU system, the dithiol system, a metal complex system, etc.

[0028] It is as follows when means forming is illustrated to said each coloring layer (1a) to said each absorption layer (1b), (2b), and (3b), (2a), and a top (3a). The specified quantity is dissolved in an organic solvent as it is, or at least three sorts of laser beam absorbents chosen first are dissolved with little coexistence of said binder resin, and each coating liquid is adjusted. Next, this each whole corresponding coloring layer top surface is coated with this each coating liquid by the coating approach (either which is illustrated in the case of said coloring layer). Stoving of after coating is carried out, it carries out evaporation removal of the organic solvent, and is completed. It is desirable to take into consideration and decide various conditions (for effect in the coloring layer by coloring of the absorbent itself to be [strong against laser beam absorbing power and an impact the adhesion force and endurance endurance,] still smaller) about the thickness of each of this absorption layer finally obtained by coating here, and it is good to decide in this by making about 0.1 micrometers - 5 micrometers into a standard. in addition, generally about an organic solvent, ether (between the shape of a chain -- or annular), fatty alcohol, ketones (the shape of a chain -- or annular), aliphatic series ester, aliphatic series nitril, and chlorinated methane are used. Moreover, it is more desirable not to ****** as much as possible, since it generally tends to worsen concomitant use of binder resin in respect of the absorption efficiency of a laser beam, the heat-conduction effectiveness to a coloring layer, the absorption peak width of face (direction to extend) of an infrared-absorption agent, etc. Especially when using it, it is good film reinforcement and to restrict, when not obtaining any longer in respect of membrane formation nature, and to make it as little as moreover possible.

[0029] Although the direct laminating of said each heat reversible color recording

layer (1), (2), and (3) will be carried out one by one on a substrate 5 and they will obtain the target heat-reversibility record medium, they once prepare this each recording layer in films, such as PET thinner than this substrate, carry out each laminating of this, and are fundamentally good also as this record medium.

[0030] Moreover, although it is a more desirable thing that it is what can record more quickly that a still clearer color image is also efficiently, and can also do a discharge, claim 2 is offered as a means for it and solution is aimed at It is said that this account means makes at least two transparence thermal breaks (4) intervene between the layers of the heat reversible color recording layer (1) which consists of at least three layers in claim 1, (2), and (3) (i.e., between (1) and (2)), and between (2) and (3). Since this transparence thermal break carries out the operation which insulates between these recording layers, heat propagation-comes to be hard of a thermal break. That is, it is used for coloring as it is, without otherwise the heat uniquely received by this recording layer of this recording layer that adjoins respectively escaping. Since affecting coloring of this recording layer that adjoins as a result, and a discharge is mitigated, a clearer color image comes to be reproduced correctly quickly. Moreover, the endurance of repeat use also improves more.

[0031] Said transparence thermal break (4) considers as about 5-100-micrometer thickness, and is specifically formed with a glass bead with a particle size of about 2-40 micrometers which forms this by the air space or contains transparence adhesive property resin etc. In the case of an air space, there are approaches, such as putting a spacer into a perimeter, considering as an entire air space, or it being extensively scattered and making a dot (point) spacer (based on transparence binder resin) with a height of 5-100 micrometers into an air space, here so that a 5-100-micrometer clearance may be vacant. Especially in the case of the latter, since an air space is certainly formed in the size of a heat-reversibility multicolor record medium not related, it is desirable. When based on a **** glass bead, this glass bead is mixed with an organic solvent using a small amount of possible transparence adhesive property resin, and the

coating (implantation) of this is carried out so that it may be extensively scattered by the detailed dot. Since it is certainly regardless of the thickness for which it asks also in this easy also for formation in the size of this record medium, it is this glass bead, and the approach of implanting this in the shape of dispersion by the dot, and forming is still more desirable.

[0032] In addition, although said obtained heat-reversibility multicolor record medium is used as it is Protecting the laser beam absorption layer which is in the maximum upper layer at least (protection from damage in environmental ambient atmospheres, such as air, water, and temperature, use, and a routing etc.) Since it is desirable, for the reason, it is transparent as much as possible, and it also good to cover extensively [about 0.1-10 micrometers of thickness] the material which also penetrates a laser beam well (it does not absorb). Although specification is not carried out as this material, when being based on resin, the coating of the precursors, such as the transparence resin of a photoresist, for example, acrylic, an epoxy system, an urethane system, an acrylic epoxy system that combines a silicone component, an acrylic urethane system, and an acrylic silicone system, is carried out, and they carry out photo-curing. On the other hand, the silicon oxide film by the sol-gel method, the oxidization silicon film by the sputtering method, or the ITO (indium stannic acid ghost) film can also be used as a protective coat. Although it is not influenced by ** and decolorization operation even if it, of course, prepares the protective layer by these, this is also because this invention changes by the specific configuration, and it is **.

[0033]

[Example] This invention is further explained in full detail according to an example with the example of a comparison below. In addition, whenever [as used in the field of in this example / coloring] is measured by the following approach, and is expressed with a L*a*b* color coordinate system. That is, JIS Irradiate the laser beam corresponding to red first, the red who did the laminating and got on the white substrate in each example, blue, and a green heat reversible 3 color record plate (medium) are made to color red using the color

color difference meter "CR-200" by Minolta Co., Ltd. currently manufactured based on Z8729, and L*a*b* of this is measured. If measurement finishes, it will heat to 80-degreeC and red will be decolorized. Next, the laser beam corresponding to blue is irradiated and it colors similarly. - It measures. - It decolorizes. The laser beam which corresponds to the last green is irradiated, and it colors, measures - decolorizes similarly. L* is so light that a figure is large at the lightness index of each color, and lacks in thickness here (if conversely small, it will become deep and will become blackish). a*b* is the chromaticity which shows a hue and ****** and, in the green direction and b*, the direction of yellow and -b* indicate [a* / the direction of red, and -a*] that the direction of blue is clear from a L*a*b* color-coordinate-system chromaticity diagram.

[0034] (Example 1) Red, blue, and the green presentation liquid for heat reversible color coloring layers were first prepared by the next formula.

For red coloring: As a heat-reversibility red color coupler, the water-solution 90 weight section of 2.5% of the weight of polyvinyl alcohol was added to 40 weight sections and this, and mixed distribution of the 2-chloro-6-diethylamino fluoro lactone fine particles was fully carried out (A liquid). On the other hand, as a developer, 2.5% of the weight of the polyvinyl alcohol water-solution 400 weight section was added to the 100 weight sections and this, and mixed distribution of the N-BEHENI roil aminophenol fine particles was fully carried out (B liquid). And this A liquid 65 weight section and this B liquid 250 weight section were extracted, and the water-solution 100 weight section of 10% of the weight of polyvinyl alcohol and the water 200 weight section were added to this, and it fully mixed, and considered as the presentation liquid for red coloring (red coloring liquid).

For blue coloring: It changed to said red color coupler, and except using 3-(4-diethylamino-2-methylphenyl)-3-(1-ethyl-2-methylindole-3-IRU)-4-aza-phthalide as a reversibility blue color coupler, it each prepared on the same conditions as the above, and the presentation liquid for blue coloring was obtained (blue coloring liquid).

Green coloring: It changed to said red color coupler, and as a reversibility green

color coupler, except using 7-(N and N-dibenzylamino)-3-(N and N-diethylamino) fluoro lactone, it each prepared on the same conditions as the above, and the presentation liquid for green coloring was obtained (green coloring liquid).

[0035] On the other hand, the presentation liquid for laser beam absorption layers corresponding to said each coloring layer was prepared by the next formula.

For red absorption: 0.1g of phthalocyanine system absorbents which absorb the wavelength of the 830nm of the maximum absorption peaks by absorption peak width of face of 50nm was dissolved in 20g of ethyl acetate (red lean solution).

For blue absorption: 0.1g of phthalocyanine system absorbents which absorb the wavelength of the 655nm of the maximum absorption peaks by absorption peak width of face of 50nm was dissolved in 20g of ethyl acetate (blue lean solution).

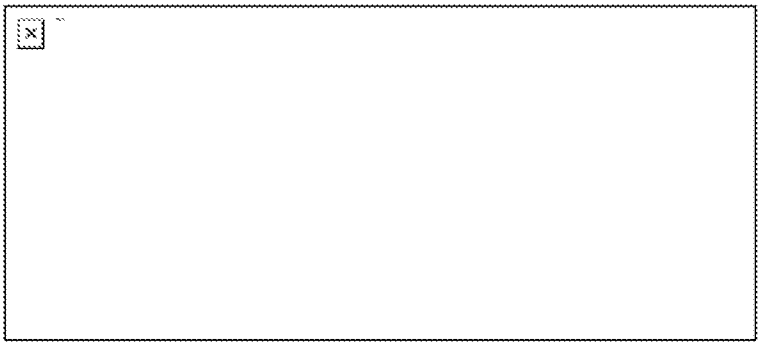
For green absorption: 0.1g of phthalocyanine system absorbents which absorb the wavelength of the 780nm of the maximum absorption peaks by absorption peak width of face of 50nm was dissolved in 20g of ethyl acetate (green lean solution).

[0036] Next, the heat-reversibility record object of three colors which carry out coating one by one, carry out the laminating of said each presentation liquid for heat reversible color coloring layers and the presentation liquid for laser beam absorption layers, and ask for them in the following procedure on this was produced by using a white opaque PET film (L^*=99.44, a^*=-0.57, b^*=0.19) with a thickness of 125 micrometers as a substrate 5. First, said red coloring liquid was applied, it dried, and 1st 10-micrometer heat reversible red coloring layer 1a was prepared, next, on this 1a, said red lean solution was applied, it dried, 1st 1-micrometer laser beam absorption layer 1b was prepared in the whole surface of this PET film, and it considered as the 1st heat reversible red recording layer 1. Next, on the heat reversible red recording layer 1, said blue coloring liquid was applied, it dried, and 2nd 10-micrometer heat reversible blue coloring layer 2a was prepared, succeedingly, said blue lean solution was applied, it dried, 2nd laser beam absorption layer 2b of 1 micrometer was prepared on this 2a, and it

considered as the 2nd heat reversible red recording layer 2. And said green coloring liquid was applied to the last on this heat reversible red recording layer 2, it dried, and 3rd 10-micrometer heat reversible blue coloring layer 3a was prepared, and on this 3a, said green lean solution was applied, it dried, 3rd 1-micrometer laser beam absorption layer 3b was prepared in the continuation, and it considered as the 3rd heat reversible green recording layer 3.

[0037] And coloring and a discharge were tested in red, blue, and green order about the heat-reversibility record object of said three produced colors, and the engine performance was checked. Coloring performed green coloring here because red coloring irradiates respectively separately the semiconductor laser light to which blue coloring has maximum single wavelength in 655nm respectively at 780nm from this record object at 830nm. After the discharge colored and measured L*a*b* whenever [coloring], before it performed the next coloring, it was performed by making it 80-degreeC. Each color was colored efficiently and the result decolorized it again. Whenever [coloring / at that time] was summarized in Table 1. Although L*a*b*-ization was measured whenever [coloring / of each color] when it was attached to ****** and coloring and a discharge were repeated 100 times, there was no difference between the beginnings (Table 1).

[0038] (Table 1)



[0039] (Example 2) (example of claim 2)

Said red coloring liquid, blue coloring liquid, green coloring liquid and the red lean solution, the blue lean solution, and the green lean solution were first prepared

on the same conditions as an example 1.

[0040] The transparence acrylic resin precursor liquid (liquid for thermal breaks) of the photoresist which, on the other hand, contains 20 % of the weight for a glass bead with a particle size of 25 micrometers as coating liquid for transparence thermal breaks was prepared, and the heat-reversibility record object of three colors with which it comes to carry out laminating mediation of this thermal break as follows using this was produced. By having used the same white PET film as an example 1 as the base, it sequential-applied, this red coloring liquid and this red lean solution were first, dried on the same conditions as this example, and the 1st heat reversible red recording layer 1 was formed. Next, at intervals of [of 5mm] the pitch, UV irradiation of this liquid for thermal breaks was implanted and carried out, it was hardened by screen printing in the shape of a grid, and the transparence thermal break 4 by the glass bead dot was formed so that it might become 27 micrometers of thickness on this red recording layer. Next, on this transparence thermal break, on the same conditions as an example 1, it sequential-applied, this blue coloring liquid and this blue lean solution were dried, and the 2nd heat reversible blue recording layer 2 was formed. And on this blue recording layer, again, UV irradiation of this liquid for thermal breaks was applied and carried out, it was hardened by screen printing, and the transparence thermal break 4 was formed so that it might become 27 micrometers of thickness. Finally, said green coloring liquid and green lean solution were applied and dried on the conditions as an example 1 that it is the same on this transparence thermal break, and the 3rd heat reversible green recording layer 3 was formed, and it ended. In addition, the configuration of the acquired heat-reversibility record object is illustrated to drawing 1 with an example 1.

[0041] And about the heat-reversibility record object which intervenes the transparence thermal break of said three obtained colors, semiconductor laser light was irradiated to each on the same conditions as an example 1, the test of coloring and a discharge was performed, and adiabatic efficiency was checked.

Consequently, when each coloring situation was first observed by the eye side, the coloring itself was sensed clearer a little than some [early and] for each color rather than the example 1. And chromaticity L*a*b* of each coloring is measured and it is **** to Table 1 about this again. A more clear thing can be proved in this table. Although L*a*b* was measured whenever [coloring / of each color] when it was attached to ****** and coloring and a discharge were repeated 150 times, the difference was not seen between the beginnings (Table 1). Moreover, when said three semiconductor laser light was irradiated at coincidence, three colors colored to coincidence in the clear color like the case of monochrome, and it also checked that the total color had decolorized shortly after setting this to 80-degreeC.

[0042] (Example 1 of a comparison) The water-solution 90 weight section of 2.5% of the weight of polyvinyl alcohol was added to 40 weight sections and this, and mixed distribution of what mixed the red color coupler, blue color coupler, and green color coupler of the heat-reversibility used in the example 1 in the amount of division into equal parts was fully carried out (C fluid). And it applied so that it might become 10 micrometers of thickness on the white PET film which used this C fluid in the example 1, and the heat reversible recording layer of 3 color mixing which dries and consists of one layer was prepared.

[0043] Next, sequential spreading was carried out using the same red lean solution, the blue lean solution, and the green lean solution, it dried and the laminating of the laser beam (2 1st, 3) absorption layer of 1-micrometer thickness was respectively carried out to having used it in the example 1 on said heat reversible recording layer.

[0044] Like the example 1, to the heat-reversibility record medium of said three obtained colors, it colored respectively, and it decolorized to it using the laser beam of a semi-conductor (655nm, 780nm, and 830nm), and the coloring situation was seen. As a result, three colors colored almost instantaneous also to the laser beam of which wavelength, and coloring in monochrome was not seen. Carry out respectively independently the laminating of a number equivalent to the

color number to color at least of the heat reversible color recording layers, and he makes this color by the laser beam which has the wavelength of a proper in coloring of the recording layer, and it can understand well that there are a heat-reversibility record medium of this invention referred to as to cool and decolorize and a remarkable difference.

[0045]

[Effect of the Invention] Since this invention is constituted as aforementioned, the following effectiveness is done so.

[0046] First, it became possible to be able to carry out multicolor coloring in a clear color very quickly by combining at least three laser beams from which wavelength differs to the heat reversible multicolor record medium in which a heat reversible recording layer comes to carry out a laminating and this medium of at least 3 colors as an independent layer respectively, and to decolorize immediately by cooling.

[0047] The periodic duty of degradation of many ** and discharges is also small, and a big improvement came to be found by endurance.

[0048] Since it wrote in by the laser beam, it came to be able to carry out a color expression to the detailed part more. The activity in the range larger than the result was attained, and possibility of taking and changing to hard copy also came out.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] A sectional view shows the heat-reversibility 3 color record medium of an example.

[Description of Notations]

1 Heat Reversible Red Recording Layer

2 Heat Reversible Blue Recording Layer

3 Heat Reversible Green Recording Layer

4 Transparence Thermal Break (Glass Bead)

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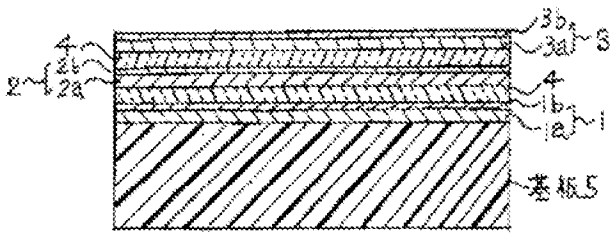
(54)【発明の名称】　熱可逆性多色記録媒体

(57)【要約】
【課題】より正確で、且つ微細で鮮明な多色画像で表現でき、そしてこれを消去する書き換え自由な新たな可逆性多色記録媒体を提供すること。
【解決手段】少なくとも３つのレーザ光を使って書き込みを行うもので、それは基板５上に少なくとも次の（Ａ）～（Ｃ）の各熱可逆カラー記録層の３層が積層されてなる熱可逆性多色記録媒体である。（Ａ）第１の熱可逆カラー発色層１ａと該発色層の発色のための波長を有する第１レーザ光の吸収層１ｂとからなる熱可逆カラー記録層１、（Ｂ）第２の熱可逆カラー発色層２ａと該発色層の発色のための波長を有する第２レーザ光の吸収層２ｂとからなる熱可逆カラー記録層２、（Ｃ）第３の熱可逆カラー発色層３ａと該発色層の発色のための波長を有する第３レーザ光の吸収層３ｂとからなる熱可逆カラー記録層３。該記録層１と２、２と３との間に透明断熱層（ガラスビーズ等）４を介在させるとより好ましい。赤、青、緑等の色で多色記録・消去が行われる。



【特許請求の範囲】
【請求項１】基板（５）上に、少なくとも次の（Ａ）～（Ｃ）の各熱可逆カラー記録層の３層が積層されてなることを特徴とする熱可逆性多色記録媒体。
（Ａ）第１の熱可逆カラー発色層（１ａ）と該発色層の発色のための波長を有する第１レーザ光の吸収層（１ｂ）とからなる熱可逆カラー記録層（１）
（Ｂ）第２の熱可逆カラー発色層（２ａ）と該発色層の発色のための波長を有する第２レーザ光の吸収層（２ｂ）とからなる熱可逆カラー記録層（２）
（Ｃ）第３の熱可逆カラー発色層（３ａ）と該発色層の発色のための波長を有する第３レーザ光の吸収層（３ｂ）とからなる熱可逆カラー記録層（３）
【請求項２】前記請求項１において、積層される少なくとも３層の熱可逆カラー記録層（１、２、３）の層間に更に透明断熱層（４）が積層されてなることを特徴とする熱可逆性多色記録媒体。
【請求項３】前記透明断熱層（４）が、厚さ５～１００μｍでドット状に植設された微細ガラスビーズによりなる請求項２に記載の熱可逆性多色記録媒体。
【請求項４】前記各熱可逆カラー発色層（１ａ、２ａ、３ａ）における色相が赤、青、緑のいずれかの３色よりなる請求項１又は２に記載の熱可逆性多色記録媒体。
【請求項５】前記各レーザ光が半導体レーザから発せられる波長６００～１０００ｎｍの光の中から選ばれる請求項１、２又は４のいずれか１項に記載の熱可逆性多色記録媒体。
【請求項６】前記各レーザ光の吸収層（１ｂ、２ｂ、３ｂ）がモル吸光係数１００００以上の赤外線吸収剤の中から各々選ばれてこれを含有してなる請求項１、２、４又は５のいずれか１項に記載の熱可逆性多色記録媒体。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】本発明は、特にレーザ書き込みに適した改良された熱可逆性多色記録媒体に関する。該記録媒体は、これ自身を書き換えのできる各種広告媒体に使用したり、書き換え又は再使用の可能な各種カード類に合体して使用することもできる。
【０００２】
【従来の技術】一般に可逆性記録媒体については、電子写真学会誌第３５巻第３号（１９９６）、１４８～１５４頁に「リライタブルマーキング技術の最近の動向」として特集解説されてもいるように、物理変化を原理として単に白濁のみの単色で画像表現する場合と、化学変化を原理として多色で画像表現する場合の２つがある。前者の単色による可逆性（リライタブル）記録媒体では、これをカード式にして既に１部ガソリンスタンド等で実用されているが、後者の多色による可逆性記録媒体ではまだ実用の段階ではないのが現状である。カラー化のニーズは高いことから、今後の大きなテーマとして研究が進められて行くものと考えられる。
【０００３】可逆性多色記録媒体について特許出願で見られる近年の技術として、例えば特開平８－８０６８２号公報を挙げることができる。該公報の基本技術思想は、各々その色特有の波長光を吸収して発熱する複数の非可逆染料（一般に印刷インキに使用されている染料又は有機顔料）を含む一層からなる着色層を下層にして、その上に特定の温度（該非可逆染料の発熱による温度）で透明又は非透明（白濁）に可逆的に変えるリライタブル層を積層して可逆性多色記録媒体とするものである。ここで該一層からなる着色層を各色層に分けて、各色層毎にその上に該リライタブル層を設け、これを透光性の断熱層（空気）を介して各々積層し該記録媒体としても良い旨も記載されている。
【０００４】
【発明が解決しようとする課題】本発明者らは、前記号公報とは異なる別の角度から種々検討してきた。その結果、より鮮明な多色画像でもって耐久性にも優れた可逆性多色記録媒体を見い出すことができ、本発明に到達した。
【０００５】
【課題を解決するための手段】即ち本発明は、まず請求項１に記載するように、基板（５）上に少なくとも次の（Ａ）～（Ｃ）の各熱可逆カラー記録層の３層が積層されてなる熱可逆性多色記録媒体を主たる手段とするものである。
（Ａ）第１の熱可逆カラー発色層（１ａ）と該発色層の発色のための波長を有する第１レーザ光の吸収層（１ｂ）とからなる熱可逆カラー記録層（１）
（Ｂ）第２の熱可逆カラー発色層（２ａ）と該発色層の発色のための波長を有する第２レーザ光の吸収層（２ｂ）とからなる熱可逆カラー記録層（２）
（Ｃ）第３の熱可逆カラー発色層（３ａ）と該発色層の発色のための波長を有する第３レーザ光の吸収層（３ｂ）とからなる熱可逆カラー記録層（３）
【０００６】そして前記主発明に関連して請求項２の発明も提供する。それは前記積層される少なくとも３層の熱可逆カラー記録層（１、２、３）の層間に更に透明断熱層（４）が積層されることを特徴とした熱可逆性多色記録媒体である。ここで該透明断熱層（４）が、好ましい形態として、厚さ５～１００μｍでドット状に植設された微細ガラスビーズにより設けらる（請求項３）。
【０００７】又前記請求項１又は２に従属して請求項４、５及び６に記載する発明も提供する。以下本発明を次の実施形態で詳述する。
【０００８】
【発明の実施の形態】まず、本発明の熱可逆性多色記録媒体（以下ＨＲＣ媒体と呼ぶ。）は、ある情報を少なくとも波長の異なる３つのレーザ（光）を使って自由に書き込み、その書き込んだ情報を３色以上の画像ですばや

く表現（顕色）する。逆にこれをある温度で急冷したり、除冷するとその表現カラー画像がそのまま維持されたり、消去されたりする。この表現と消去の繰り返し動作のできる、つまりリライタブルカラー情報記録媒体を新たな構成によって可能にしたものと言える。

【０００９】ここで特に書き込みをレーザ光に特定しているのは、他の例えばサーマルヘッドからの熱放出とか、磁気、電界、圧力等による書き込み方法に比較してより微細な画像が、より鮮明に迅速に書き込まれることと、非接触状態で配置できるということで、汚れや損傷等の危険性もないためである。

【００１０】そこで前記少なくとも３つのレーザ光による書き込み可能なＨＲＣ媒体はどのような構成によっているかを、請求項１に基づいて説明する。

【００１１】まずＨＲＣ媒体は、安全で取り扱いやすく（製造上、使用上）するために基板５上に設けられる。該基板の使用形態（素材、厚さ、透明～不透明、用途等）は、例えば次のとおりである。素材については、例えば板紙、合成紙、合成繊維による不織布、ポリエチレンテレフタレート、ポリエチレンナフタレート、ポリエーテルケトン、ポリカーボネート、ポリメチルメタクリレート、環状ポリオレフィン、ポリエーテルスルホン、ポリアリレート等の結晶性又は非晶性の熱可塑性樹脂によるシート状物、エポキシ系、アクリル系、ウレタン系、イミド系等の熱硬化性樹脂によるシート状物、セラミック、ガラス等の無機のシート状物が挙げられる。勿論これら適宜２種以上を複合した複合シートであっても良い。これらの厚さは、一般に約０．１～３ｍｍとされる。また透明～（半透明）～不透明については、これは特に用途との関係で決められる。例えば、ポスタ等のディスプレイ的な用途では透明ないし半透明のシート、各種カード類との合体では、不透明のシートを選ぶ。そして、これらが透明な場合は無着色であり、半透明～不透明な場合は白色系であることが好ましい。白色化は、酸化チタンによる練り込み又は表面コーテング、表面粗化等の方法がある。尚、前記シートに接着性を付与するために、物理的（コロナ放電等）、化学的（酸化剤による表面酸化等）方法によって前処理を行ってもよいし、必要ならアンカーコート層を設けてもよい。

【００１２】そして前記基板５上に少なくとも（Ａ）～（Ｃ）の熱可逆カラー記録層（１）、（２）、（３）が各々独立して積層されるが、これは少なくとも波長の異なる３つのレーザ光を使って、少なくとも各々３色で画像表現するためである。従って特に（Ａ）を第１、（Ｂ）を第２、（Ｃ）を第３と呼称しているのは、これら少なくとも３つに区別するために呼ぶ便宜的なものであり、積層（該記録層－色相）の順序を言っているものでもない。尚該記録層の積層順序は、視認性のより向上の点から濃色系を最下層にして、順次上に淡い色が積層されてなるようにするのが好ましい。例えば赤、青、緑又は黄の３色相の場合では赤を最下層に、青を中間層に、緑又は黄を最上層にする。

【００１３】前記少なくとも第１、第２、第３における熱可逆カラー記録層（１、２、３）は、各々に対応して熱可逆カラー発色層（１ａ、２ａ、３ａ）とレーザ光吸収層（１ｂ、２ｂ、３ｂ）とからなっている。次にこの各該発色層と吸収層について詳述する。

【００１４】まず前記各熱可逆カラー発色層は、例えば赤、青、緑の３色相で色表現する場合、各々の発色源である電子供与性染料の前駆体（以下発色剤と呼ぶ。）と、該発色剤に対して温度と共に顕減色作用をする電子受容性化合物（以下顕色剤と呼ぶ。）の両者を主成分とし、これをバインダー樹脂に混合し分散して各該層としている。ここで該樹脂の存在は、発色と消色のより鮮明で忠実な繰り返し作用の面からは、無い方が好ましい。しかし発色剤と顕色剤とを均一に分散し、基板５との密着性を強固なものにするためには、該樹脂の併用が望ましい。但し、その組成量は、可能な限り少量であることが望ましい。

【００１５】前記発色剤としては、例えば赤色では２－クロロー６－ジエチルアミノフルオランラクトン、３－メチルー６－ジエチルアミノフルオランラクトン等のフルオランラクトン化合物。青色では、３－（４－ジエチルアミノー２－メチルフェニル）－３－（１－エチルー２－メチルインドールー３－イル）－４－アザフタリド、３－（４－ジエチルアミノー６－エトキシフェニル）－３－（１－ヘキシルー２－メチルインドールー３－イル）－４－アザフタリド等のフタリド系化合物。緑色では、７－（Ｎ，Ｎ－ジベンジルアミノ）－３－（Ｎ，Ｎ－ジエチルアミノ）フルオランラクトン、７－（Ｎ－オクチルアミノ）－３－（Ｎ，Ｎ－ジエチルアミノ）フルオランラクトン等のフルオランラクトン化合物。他に黄色では、３－メトキシー６－メトキシフルオランラクトン等のフルオランラクトン化合物、黒色では、７－（２－クロルフェニルアミノ）－３－（ジエチルアミノ）フルオランラクトン、６－メチルー７－（２，４－ジメチルフェニルアミノ）－３－（ジエチルアミノ）フルオランラクトン等のフルオランラクトン化合物が例示できる。勿論これらは常態では、無色又は淡着色をしていて、常態で各々着色しているインキ用染料、顔料とは異なっている。

【００１６】また、前記顕色剤は、基本的には、前記発色剤を発色させる顕色能を示す構造部分と、分子間の凝集力をコントロールする長鎖脂肪族構造部分とを合わせ有する化合物であれば特に制限するものはない。例えば、該顕色能を示す構造部分ではリン酸基、カルボン酸基、芳香族基等で、該凝集力をコントロールする構造部分では炭素数Ｃ１０以上、好ましくはＣ１２～Ｃ２４の長鎖アルキル基である。具体的化合物を例示すると、Ｎ－ベヘニロイルー４－アミノフェノール、ｐ－（オクタ

デシルチオ）フェノール、ｐ－（エイコシルオキシ）フェノール、ｐ－ヘキサデシルカルバモイルフェニール、４－（Ｎ－ベヘノイルアミノ）フエノキシ酢酸等の長鎖アルキル芳香族系化合物、α－ヒドロキシヘキサデカン酸、２－ブロモヘキサデカン酸、３－オキソオクタデカン酸、オクタデシルリンゴ酸、オクタデシルチオリン酸、２－オクタデシルペンタニン酸等の長鎖アルキルモノ又はジカルボン酸化合物、オクタデシルホスホン酸、エイコシルホスホン酸等の長鎖アルキルリン酸化合物等を挙げることができる。

【００１７】又前記バインダー樹脂としては、まず発色剤と顕色剤とに対して相容性があり、基板５との密着性に優れ、溶剤（水または有機溶剤）に溶解し、それ自身の透明、耐熱及び耐候性にも優れている樹脂ということを考慮して選択するのがよい。かかる条件の樹脂に適合する樹脂は種々考えられるが、非晶性の熱可塑性ポリマの中で選ぶのがより好ましい。

【００１８】前記バインダー樹脂としての非晶性の熱可塑性ポリマは、例えばポリ塩化ビニル、ポリ酢酸ビニル、ポリ塩化ビニルと酢酸ビニルの共重合ポリマ、ポリスチレン又はこれと他のビニルモノマとの共重合ポリマ、アクリル系の単独又はこれと他のビニルモノマとの共重合ポリマ、マレイン酸系共重合ポリマ、ポリビニルアルコール系ポリマ、環状オレフィン系ポリマ等のビニル系ポリマ、フェノキシポリマ、ポリウレタン、ポリカーボネート、エステル系ポリマ（非晶性）、半合成セルロース（エチルセルロース、ヒドロキシエチルセルロース、カルボキシメチルセルロース）、デンプン等を挙げることができる。尚、あえて結晶性の熱可塑性ポリマを使用する場合には、可能なかぎり結晶化度が低く、融点の低いものを選ぶのがよい。

【００１９】前記各熱可逆カラー発色層を構成する前記何れかの発色剤、顕色剤及びバインダー樹脂の組成割合は、種々の条件を勘案して、予備実験により決定するのがよいが、大略次の通りである。発色剤15～40重量％、顕色剤85～60重量％そして、バインダー樹脂は、発色剤と顕色剤との合計量に対して1～10重量％。尚、該発色層の形成特性や発色／消色特性等の改善のために、例えば分散剤、界面活性剤、滑剤、酸化防止剤、紫外線吸収剤、光安定剤、発色安定剤、消色促進剤、一般の感熱紙に使われるような増感剤等の添加剤の微量添加は許容される。

【００２０】そして前記各熱可逆カラー発色層の基板上への形成手段は、一般には次の方法が採られる。まず所望量の樹脂バインダーを有機溶剤に溶解する。溶解量は、該樹脂に対する溶解性とか形成方法によって異なるので一義的に決められないので、予備テストによって決めるのが良い。次に溶解された溶液中に所定の発色剤と顕色剤の必要量を各々別個又は両者予め混合したものを添加する。添加後は、十分に攪拌し全体を均一に分散する。ここで、混合条件にも、混合順序にも制限はない。そしてコーテイング手段（スピンコーテイング、ロールコーテイング、スプレーコーテンイグ、スクリーン印刷法等）により所定厚さに塗布し、乾燥する。

【００２１】ここでコーテイングする前記各発色層の層厚は、これを最下層にするか、中間層にするか、最上層にするかによって変えることが好ましい。これは上層が厚いとレーザ光の透過を悪くし、その結果表示される画像の発色濃度、シャープ差等に悪影響がでやすくなるからである。だからと言ってあまりに薄くすることは、その層自身の発色濃度を下げることになる。従って、かかることに留意し事前チェックにより決めるのがよいが、一般的に言える範囲は、1～30μm、好ましくは５～２０μmであり、この中で各発色層に最適な層厚を見出す。

【００２２】次に前記各熱可逆カラー発色層（１ａ）（２ａ）（３ａ）に対応して設ける第１、２、３のレーザ光の吸収層（１ｂ）、（２ｂ）、（３ｂ）について詳述する。

【００２３】前記各吸収層は、各々波長の異なる第１、第２又は第３のレーザ光をすばやく吸収し熱（所定温度）に変換し、そしてこれを各々の前記発色層に忠実に、且つ高効率で伝達するに必要なものである。従って該吸収層は、該発色層をどのような色相にするかによって決まり、レーザ光（波長）も決まることになる。これは逆に各々の使うレーザ光の波長を決めれば該吸収層、それに対する該発色層も決まることにもなる。尚該吸収層の色味と発色層の色味とは可能な限り合わせるようにするのがよい。

【００２４】ここでまず使用するレーザ光は、一般に約６００～１０００ｎｍ、好ましくは６５０～９００ｎｍの波長域を有するものが選択され、更にこの波長域内で決められた波長は可能な限り単波長であるのがよい。尚該レーザ光の発生源は、ガスレーザ、固定レーザ、半導体レーザ等が対象になるが、中でも光出力２０ｍＷ程度の半導体レーザが好ましい。

【００２５】そして前記決められた各レーザ光に対しての前記各吸収層は、具体的には次のような内容のものである。まず該層は、選択されたレーザ光からの波長を選択的に高効率で吸収し、そのまま所定の熱（温度）エネルギーに変換することのできるレーザ光吸収剤が主成分となって形成される。ここでかかる吸収剤のより有効な選択は、前記決められた各発色層の発色色度への影響、耐久性（反復加熱と冷却に対する耐熱性）、製膜性、発色層との密着性等を考慮して決めるのは勿論であるが、更にモル吸光係数も考慮することも好ましいことである。

【００２６】前記モル吸光係数（分子吸光係数ともいう。）は、一般に色素分子が光を吸収する強さと表現されるが、本発明においては、前記吸収剤分子がレーザ光から発せられる６００～１０００ｎｍ（可視ないし赤外

線波長）の範囲の中での吸収の強さということになる。そして、これはＪＩＳ　Ｋ０２１２に記載される吸光度測定法によって測定することができる。このモル吸光係数も加味すると、該吸収剤は数字的には10000以上のレーザ光吸収剤、より好ましくは20000以上の該吸収剤であり、更には特定されるレーザ光に対して、吸収波長ピークの幅が２００ｎｍ以下のものであることも条件に入れると、より一層好ましい赤外線吸収剤を選ぶことができる。

【００２７】対象となる前記レーザ光吸収剤を系類別に例示すると、一般に知られているシアニン系、フタロシアニン系、インドシアニン系、ナフタロシアニン系、アントラキノン系、ポリメチン系、アミニウム系、イモニウム系、ジチオール系、金属錯体系等で、この中で更に前記条件を基に、前記発色層の発色に特有の熱変換波長のみを吸収する該吸収剤を選ぶことになる。

【００２８】前記各吸収層（１ｂ）、（２ｂ）、（３ｂ）への前記各発色層（１ａ）、（２ａ）、（３ａ）上へ形成手段を例示すると次の通りである。まず選択された少なくとも３種のレーザ光吸収剤をそのまま有機溶媒に所定量を溶解するか、又は前記バインダー樹脂の少量の共存と共に溶解して各塗布液を調整する。次に該各塗布液を対応する該各発色層上全面に、（前記発色層の場合に例示するいずれかの）コーテイング方法でコーテイングする。コーテイング後は加熱乾燥して有機溶媒を蒸発除去し終了する。ここでコーテイングによって最終的に得る該各吸収層の層厚については、種々の条件（レーザ光吸収能、衝撃に強い密着力と耐久性、更には吸収剤自身の着色による発色層への影響の小さいこと等）を勘案して決めることが好ましく、それは約0.1μm～5μmを目安としてこの中で決めると良い。尚有機溶剤については、一般にエーテル類（鎖状間又は環状）、脂肪族アルコール類、ケトン類（鎖状又は環状）、脂肪族エステル類、脂肪族ニトリル類、塩素化メタン類等が使用される。又バインダー樹脂の併用は、一般にはレーザ光の吸収効率、発色層への熱伝導効率、赤外吸収剤の吸収ピーク幅（広げる方向）等の点では悪くする傾向があるので、可能なかぎりり使用しない方が望ましい。使用する場合は、特に膜強度とか、成膜性の点でやもう得ない場合に限り、しかも可能な限り少量にするのが良い。

【００２９】前記各熱可逆カラー記録層（１）、（２）、（３）は、基本的には基板５上に順次直接積層されて目的の熱可逆性記録媒体を得ることになるが、各々の該記録層を一旦該基板よりもより薄いＰＥＴ等のフイルムに設けて、これを各積層して該記録媒体としても良い。

【００３０】又より一層鮮明な色画像でもってより迅速に効率良く記録でき、また消色もできるものであることはより望ましいことであり、そのための手段として請求項２を提供し解決をはかるが、該記手段は、請求項１における少なくとも３層からなる熱可逆カラー記録層（１）（２）（３）の層間、つまり（１）と（２）との間と、（２）と（３）との間に少なくとも２つの透明断熱層（４）を介在させると言うものである。この透明断熱層は、該記録層間を断熱する作用をするので、熱が伝わりにくくなる。つまり各々隣接する該記録層の該記録層で独自に受けた熱が他に逃げることなく、そのまま発色に利用される。その結果隣接する該記録層の発色、消色に影響を及ぼすことが軽減されるので、より鮮明な色画像が迅速に、正確に再現されるようになる。又繰り返し使用の耐久性もより向上する。

【００３１】前記透明断熱層（４）は、具体的には５～１００μm程度の層厚とし、これを空気層で形成するとか、透明接着性樹脂を含む粒径２～４０μm程度のガラスビーズ等で形成する。ここで空気層の場合は、例えば５～１００μmの隙間が空くように周囲にスペーサを入れて全くの空気層とするか、高さ５～１００μmのドット（点）スペーサ（透明バインダー樹脂による）を全面的に散在して空気層とする等の方法がある。特に後者の場合には、熱可逆性多色記録媒体のサイズに関係なく確実に空気層が形成されるので好ましい。又該ガラスビーズによる場合は、可能なかぎり少量の透明接着性樹脂を使って有機溶剤と共に該ガラスビーズを混合し、これを全面的に又は微細ドットで散在するようにコーテング（植設）する。この中でも所望する層厚が該記録媒体のサイズに関係なく確実に、且つ形成にも容易である理由から該ガラスビーズで、更にはこれをドットで散在状に植設して形成する方法が好ましい。

【００３２】尚前記得られた熱可逆性多色記録媒体は、そのまま使用するが、少なくとも最上層にあるレーザ光吸収層を保護（空気、水、温度等の環境雰囲気、使用中、作業工程中での損傷等からの保護）することは、好ましいことであるので、その為に可能なかぎり透明でレーザ光も良く透過（吸収せず）する素材を、膜厚0.1～10μm程度全面的に被覆するのも良い。該素材としては特定はしないが樹脂による場合は、光硬化性の透明樹脂、例えばアクリル系、エポキシ系、ウレタン系、シリコーン成分を結合するアクリル・エポキシ系、アクリル・ウレタン系、アクリル・シリコーン系等の前駆体をコーテングし光硬化する。一方ゾル・ゲル法による酸化ケイ素膜、スパッタリング法による酸化珪素膜またはＩＴＯ（インジウム錫酸化物）膜等を保護膜とすることもできる。勿論これらによる保護層を設けても発・消色作用には影響されないが、これも本発明が特定の構成によって成っているためであ。

【００３３】

【実施例】以下に本発明を比較例と共に、実施例によって更に詳述する。尚、該例中でいう発色度は次の方法によって測定しＬ＊ａ＊ｂ＊表色系で現したものである。つまりＪＩＳ　Ｚ８７２９に基づいて製作されているミ

ノルタ株式会社製の色彩色差計“ＣＲ－２００”を用いて、各例において白色基板上に積層して得た赤、青、緑の熱可逆３色記録板（媒体）に、まず赤に対応するレーザ光を照射し赤を発色させてこれのＬ＊ａ＊ｂ＊を測定する。測定が終わったら８０°Ｃに加熱して赤を消色する。次に青に対応するレーザ光を照射し同様に発色－測定－消色。最後に緑に対応するレーザ光を照射し同様に発色－測定－消色する。ここでＬ＊は各色の明度指数で数字が大きい程淡く、濃さに欠ける（逆に小さいと濃くなり黒っぽくなる）。ａ＊ｂ＊は、色相と彩度ををを示す色度で、Ｌ＊ａ＊ｂ＊表色系色度図から明らかなようにａ＊は赤方向、－ａ＊は緑方向、そしてｂ＊は黄方向、－ｂ＊は青方向を示している。

【００３４】（実施例１）まず、次の処方で赤、青、緑の熱可逆カラー発色層用組成液を調製した。

赤発色用：熱可逆性赤色発色剤として2-クロロ-6-ジエチルアミノフルオロラクトン粉体を40重量部、これに2.5重量%のポリビニルアルコールの水溶液90重量部を添加し、十分に混合分散した（Ａ液）。一方顕色剤としてN-ベヘニロイルアミノフェノール粉体を100重量部、これに2.5重量%のポリビニルアルコール水溶液400重量部を添加し、十分に混合分散した（Ｂ液）。そして該Ａ液６５重量部、該Ｂ液250重量部を採取しこれに１０重量%のポリビニルアルコールの水溶液100重量部及び水200重量部を添加し十分に混合して赤発色用組成液とした（赤発色液）。

青発色用：前記赤色発色剤に替えて、可逆性青色発色剤として3-（4-ジエチルアミノ-2-メチルフェニル）-3-（1-エチル-2-メチルインドール-3-イル）-4-アザフタリドを用いる以外は、前記と同一条件で各調製して青発色用組成液を得た（青発色液）。

緑発色：前記赤色発色剤に替えて、可逆性緑色発色剤として、7-（N,N-ジベンジルアミノ）-3-（N,N-ジエチルアミノ）フルオロラクトンを用いる以外は、前記と同一条件で各調製して緑発色用組成液を得た（緑発色液）。

【００３５】一方前記各発色層に対応するレーザ光吸収層用組成液を次の処方で調製した。

赤吸収用：吸収ピーク幅５０ｎｍで最大吸収ピーク８３０ｎｍの波長を吸収するフタロシアニン系吸収剤0.1gを酢酸エチル20ｇに溶解した（赤吸収液）。

青吸収用：吸収ピーク幅５０ｎｍで最大吸収ピーク６５５ｎｍの波長を吸収するフタロシアニン系吸収剤0.1gを酢酸エチル20gに溶解した（青吸収液）。

緑吸収用：吸収ピーク幅５０ｎｍで最大吸収ピーク７８０ｎｍの波長を吸収するフタロシアニン系吸収剤0.1gを酢酸エチル20ｇに溶解した（緑吸収液）。

【００３６】次に厚さ１２５μｍの白色不透明ＰＥＴフイルム（Ｌ＊＝９９．４４，ａ＊＝－０．５７，ｂ＊＝０．１９）を基板５として、この上に前記各熱可逆カラー発色層用組成液及びレーザ光吸収層用組成液とを、下記の手順で順次コーテングし積層して所望する３色の熱可逆性記録体を作製した。該ＰＥＴフイルムの全面に、まず前記赤発色液を塗布、乾燥して１０μｍの第１熱可逆赤発色層１ａを設け、次に該１ａの上に前記赤吸収液を塗布、乾燥して１μｍの第１レーザ光吸収層１ｂを設け第１の熱可逆赤記録層１とした。次に熱可逆赤記録層１上に前記青発色液を塗布、乾燥して１０μｍの第２熱可逆青発色層２ａを設け、引続き該２ａの上に前記青吸収液を塗布、乾燥して１μｍの第２レーザ光吸収層２ｂを設け第２の熱可逆赤記録層２とした。そして最後に該熱可逆赤記録層２上に前記緑発色液を塗布、乾燥して１０μｍの第３熱可逆青発色層３ａを設け、続きに該３ａの上に前記緑吸収液を塗布、乾燥して１μｍの第３レーザ光吸収層３ｂを設け第３の熱可逆緑記録層３とした。

【００３７】そして前記作製した３色の熱可逆性記録体について赤、青、緑の順で発色・消色のテストを行い性能を確認した。ここで発色は赤発色は８３０ｎｍに、青発色は６５５ｎｍに、緑発色は７８０ｎｍに各々最大単波長をもつ半導体レーザ光を各々別個に該記録体の上から照射することで行った。消色は発色して発色度Ｌ＊ａ＊ｂ＊を測定してから次の発色を行う前に８０°Ｃにすることで行った。結果は各色共に効率良く発色し又消色した。その時の発色度を表１にまとめた。尚各色に付き発色と消色とを１００回繰り返した時点で各色の発色度Ｌ＊ａ＊ｂ＊化を測定したが、最初（表１）との間に差はなかった。

【００３８】（表１）

実施例　NO	発色	L*	a*	b*
1	赤	84．53	18．40	16．23
	青	89．65	−4．99	−8．86
	緑	63．47	−12．20	6．05
2	赤	82．95	20．43	16．34
	青	88．82	−6．48	−9．21
	緑	60．18	−14．37	6．21

【００３９】（実施例２）（請求項２の例）　まず実施例１と同一条件にて、前記赤発色液、青発色

液、緑発色液及び赤吸収液、青吸収液、緑吸収液を調製した。

【００４０】一方透明断熱層用の塗布液として粒径２５μｍのガラスビーズを２０重量％を含む光硬化性の透明アクリル系樹脂前駆体液（断熱層用液）を調製し、そしてこれを使って次のようにして該断熱層が積層介在されてなる３色の熱可逆性記録体を作製した。実施例１と同じ白色ＰＥＴフイルムを基体として、該例と同じ条件でまず該赤発色液と該赤吸収液とを順次塗布・乾燥して、第１の熱可逆赤記録層１を設けた。次に該赤記録層上に層厚２７μｍになるように、該断熱層用液をピッチ間隔５ｍｍで格子状にスクリン印刷にて植設し、紫外線照射して硬化しガラスビーズドットによる透明断熱層４を設けた。次に該透明断熱層の上に、実施例１と同じ条件で該青発色液と該青吸収液とを順次塗布・乾燥して、第２の熱可逆青記録層２を設けた。そして該青記録層上に層厚２７μｍになるように、再度該断熱層用液をスクリン印刷にて塗布し、紫外線照射して硬化して透明断熱層４を設けた。最後に該透明断熱層の上に実施例１と同じ条件で前記緑発色液と緑吸収液とを塗布・乾燥して第３の熱可逆緑記録層３を設けて終了した。尚得られた熱可逆性記録体の構成を実施例１と共に図１に図示する。

【００４１】そして前記得た３色の透明断熱層を介在する熱可逆性記録体について、実施例１と同一条件で各々に対して半導体レーザ光を照射し、発色と消色のテストを行い断熱効果の確認を行った。その結果、まず各発色状況を目側で観察すると、各色共に実施例１よりも発色そのものが若干早く、且つ若干より鮮明に感じられた。そして各発色の色度Ｌ＊ａ＊ｂ＊を測定しこれを表１にまとめた。この表でより鮮明であることが立証できる。尚各色に付き発色と消色とを１５０回繰り返した時点で、各色の発色度Ｌ＊ａ＊ｂ＊を測定したが、最初（表１）との間に差は見られなかった。又前記３つの半導体レーザ光を同時に照射したところ、単色の場合と同じように鮮明な色で３色が同時に発色し、そしてこれを８０°（にすると直ちに全色が消色したことも確認した。

【００４２】（比較例１）実施例１で使用した熱可逆性の赤色発色剤と青色発色剤と緑色発色剤とを等分量で混合したものを４０重量部、これに２．５重量％のポリビニルアルコールの水溶液９０重量部を添加し十分に混合分散した（Ｃ液）。そして該Ｃ液を実施例１で用いた白色ＰＥＴフイルムに層厚１０μｍになるように塗布し、乾燥して１層からなる３色混合の熱可逆記録層を設けた。

【００４３】次に前記熱可逆記録層の上に、実施例１で使用したと同一の赤吸収液、青吸収液、緑吸収液を使って順次塗布し、乾燥して各々１μｍ層厚のレーザ光（第１、２、３）吸収層を積層した。

【００４４】前記得られた３色の熱可逆性記録媒体に、実施例１と同様に６５５ｎｍ、７８０ｎｍ、８３０ｎｍの半導体のレーザ光を使って各々発色し、また消色して発色状況を見た。その結果いずれの波長のレーザ光に対しても３色がほぼ同時的に発色してしまい、単色での発色は見られなかった。少なくとも発色したい色数に相当する数の熱可逆カラー記録層を各々独立して積層し、これをその記録層の発色に固有の波長を持つレーザ光で発色させ、また冷却して消色すると言う本発明の熱可逆性記録媒体と顕著な差のあることがよく理解できる。

【００４５】

【発明の効果】本発明は前記の通り構成されているので、次のような効果を奏する。

【００４６】まず、各々単独層として少なくとも３色の熱可逆記録層により積層されてなる熱可逆多色記録媒体と、該媒体に対して波長の異なる少なくとも３つのレーザ光を組み合わせることで極めて迅速に、鮮明な色で多色発色させることができ、そして冷却することで直ちに消色することが可能になった。

【００４７】多数回の発・消色の反復使用でも性能低下が小さく、耐久性に大きな改善が見られるようになった。

【００４８】レーザ光で書き込みを行うので、より微細部分までカラー表現できるようになった。その結果より広い範囲での活用が可能になり、ハードコピーに取って変わる可能性も出てきた。

【図面の簡単な説明】

【図１】実施例の熱可逆性３色記録媒体を断面図で示す。

【符号の説明】

１　熱可逆赤記録層
２　熱可逆青記録層
３　熱可逆緑記録層
４　透明断熱層（ガラスビーズ）

【図１】